

RAMAN-, LEED- AND AUGER SPECTROSCOPY OF CLEAN AND
OXIDIZED (110)-GaAs-SURFACES

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Raman-, LEED- and Auger spectroscopy (AES) have been combined in a single ultra-high vacuum apparatus to study the band bending on in-situ cleaved (110)-surfaces of n-GaAs as a function of doping, cleavage conditions and oxygen exposure. Starting at a clean surface with flat band conditions, the measurement of a bulk phonon property, i.e. the resonantly at the E_1 -gap (2.941 eV) excited symmetry forbidden LO-Raman intensity shows via its dependence on the surface electric field a stepwise increase of the band bending for oxygen exposures of 10L, 4×10^2 L and 6×10^3 L, not observed previously with other techniques.

I. Introduction

The aim of this contribution is to demonstrate the usefulness of bulk phonon Raman spectroscopy for the study of surface band bending on polar semiconductors. We have chosen the case of O_2 on clean GaAs to compare our results with the ones obtained with other techniques.

Concerning the clean, UHV-cleaved (110)-surface of GaAs, the techniques of contact potential difference (CPD) measurements [1], UV-excited photoemission spectroscopy (UPS) [2] and photoemission yield spectroscopy [3], consistently yield at least three sets of samples (classified as "very good, good and bad" cleaves) with either no surface band bending or surface Fermi level (E_{FS}) positions with discrete values between about 0.1 eV below the conduction band minimum and midgap for n-type samples. The origin of these differences is associated with extrinsic surface defect induced effects [3] or surface strain [2]. Depending on the starting value of E_{FS} , the different sets of samples also show a different behaviour when exposing the clean surface to small doses of O_2 ($0-10^3$ L) [2,3], whereas all samples reach an E_{FS} -position at about midgap after high O_2 exposures beyond 10^6 L.

From the measurement of symmetry forbidden LO phonon Raman scattering, resonantly excited at the E_1 -gap of GaAs, one can detect - via its dependence on the surface electric field - changes in the surface band bending. We have exploited this technique to deduce more detailed information about the variation of E_{FS} as a function of cleavage condition, n-type doping and O_2 dose, especially in the low exposure regime ($\lesssim 10^4$ L).

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II. Experimental Techniques

The samples used were single crystals of GaAs with bulk carrier concentrations of $n = 1.6 \times 10^{16} - 5 \times 10^{18} / \text{cm}^3$. (110)-surfaces were obtained by cleaving the samples in air or inside an UHV-system, which also allowed for surface and residual gas analysis by means of LEED, AES and ion mass spectroscopy. For the measurement of Raman spectra, the sample can be transferred inside the UHV-system into the center of a hemispherical optical window. The Raman spectra have been obtained in backscattering geometry using a Kr^+ ion laser or a UV-pumped Stilbene 1 dye laser with photon energies in the range 2.7-3.0 eV (around the E_1 -gap of GaAs) and a conventional double holographic grating spectrometer with photomultiplier and associated photon counting electronics. The exciting laser beam can be focussed onto the sample surface in a slit or spot image of about 100 μm in diameter, thus allowing to study the surface with a relatively high spatial resolution. The laser power (10-20 mW) was kept low enough, in order to avoid effects of screening by photoexcited carriers.

III. Experimental Results and Discussion

In principle, Raman scattering by LO phonons in GaAs is symmetry forbidden in the backscattering geometry from (110) surfaces. Close to resonance, however, when the exciting photon energy is about equal to electronic interband transitions, other symmetry breaking mechanisms are responsible for the observation of "forbidden" LO phonon scattering. Three such processes have been discussed in the literature [4]:

- 1) intraband scattering of electrons by LO phonons with finite q-vectors caused by the Fröhlich interaction
- 2) forbidden LO phonon scattering induced by impurities
- 3) forbidden LO phonon scattering induced by a surface electric field.

In Figure (1) the TO and LO phonon Raman spectra are shown for a medium n-type Si-doped sample with the excitation energy of $h\nu = 2.941$ eV chosen at the top of the E_1 -gap resonance. In the scattering configuration used, Raman scattering by TO phonons is allowed and independent of the surface electric field. Thus, both the spectra from a "clean", UHV-cleaved sample with no Fermi level pinning and from an "oxidized", air cleaved sample have been normalized to the TO intensity. There is an increase of the LO phonon intensity due to the presence of the surface electric field on the pinned air-cleaved sample. But one observes also a LO phonon-like peak under flatband conditions, where in principle the LO phonon should be screened by the carriers present up to the surface, and coupled LO phonon-plasmon modes should be observed at different frequencies assuming wave-vector conservation. However, scattering processes involving wave-vector non-conservation with q-transfers larger than the Thomas-Fermi screening vector q_{TF} apparently give rise to the observation of a nearly unscreened LO phonon. In our case, q nonconserving processes can be attributed either to impurity induced scattering or to the strong absorption of the incoming light within $\sim 150 \text{ \AA}$ [5].

Similar spectra have been taken for different n-type doping levels [6]. In all cases one observes a LO phonon like peak under flatband conditions which increases with increasing doping atom concentration, thus pointing to the influence of the above mentioned process of q-nonconserving impurity induced scattering. Analyzing the relative increase of the normalized LO intensity between a flatband and a pinned surface (E_{FS} at midgap) as a function of the

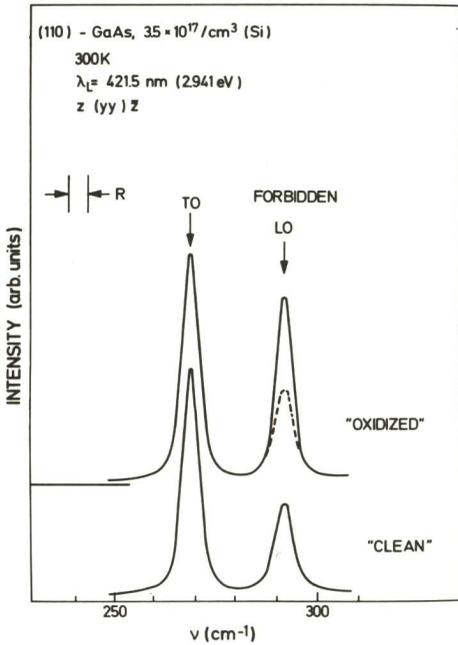


Fig. 1 Raman spectra of clean and air-cleaved n-GaAs

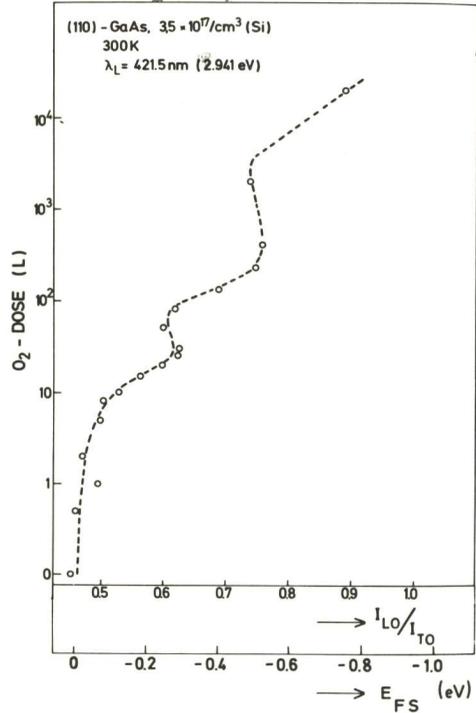


Fig. 2 Dependence of the LO phonon intensity on the O_2 exposure

carrier concentration within the framework of the Schottky barrier model, one finds the expected quadratic dependence of the LO intensity on the calculated surface electric field as long as the light penetration depth is smaller than the field penetration depth [6].

For a medium bulk carrier concentration of $3.5 \times 10^{17}/\text{cm}^3$, the variation of the normalized LO intensity as a function of the O_2 exposure is shown in Fig. (2). From cleave to cleave and in some cases by moving the sampling laser spot on the same clean "optically perfect" surface, we observed two sets of I_{LO}/I_{TO} -values at 0.46 and 0.53 but never a value of 0.84 corresponding to the air-cleaved sample. Since the barrier height Φ_B and E_{FS} vary linearly with I_{LO}/I_{TO} and by taking the two fix points $\Phi_B=0$ for $I_{LO}/I_{TO}=0.46$ and $\Phi_B=0.65$ V for $I_{LO}/I_{TO}=0.84$ on the air-cleaved sample, one can translate the I_{LO}/I_{TO} -scale in an E_{FS} -scale relative to the conduction band minimum (see Fig.(2)).

Starting now with flatband conditions on the clean surface, we observe a stepwise shifting of E_{FS} at about 10L, 4×10^2 L and 6×10^3 L. Care was taken to avoid artifacts due to the experimental procedure. The Raman spectra were repetitively scanned while admitting research grade O_2 to the UHV-system with all exciting sources in the system except the ion sputter pump turned off. This procedure was chosen after extensive ion mass spectroscopy to get the highest ratios between O_2 and residual gases (mainly H_2 and CO) while accepting about 10-15% atomic oxygen. The partial pressure of O_2 was 5×10^{-9} T for exposures up to 50L and ranged up to 5×10^{-6} T for exposures beyond 5×10^3 L. It was changed only after the completion of a step in $I_{LO}/$

I_{TO} .

Simultaneously, the 1x1 LEED pattern could be followed with decreasing spot to background ratio but no change in structure up to O_2 -exposures of 10^4L , whereas with AES a measurable O-KLL transition only appears for O_2 -exposures beyond 10^3L together with changes in the MVV transitions of Ga and As, thereby indicating that the first two band bending steps take place at oxygen coverages of less than 0.01 monolayers.

Additionally, two observations are worth noting. First, the initial step in E_{FS} at 10L is reversible when turning off the O_2 leak after completion of the step and it can be "retarded" by increasing the power density of the exciting laser beam. Second, samples which were processed through the steps showed after taking them back out in air an I_{LO}/I_{TO} -value of 1.1 and by recleaving the same sample in air again the usual value of 0.84. This behaviour indicates that one can move E_{FS} about 1 eV below the conduction band minimum in n-GaAs under suitable surface treatment.

The stepwise nature of the shifting of E_{FS} demonstrates that several discrete physical changes and/or surface chemical reactions - some of them reversible in nature - take place during the O_2 -exposure at surface coverages less than 1 oxygen atom per 100 substrate atoms. Besides the above mentioned oxygen induced surface defect and surface strain relief mechanism one has to consider also weakly bound physisorption states of molecular and atomic oxygen which could be reversible under varying external parameters, e.g. the laser power density. One can also think about the importance of the doping atoms for the surface chemistry, since the calculated values for the surface charge, necessary to compensate the space charge in the depletion layer for a given barrier height, are of the same order of magnitude as the minimum surface concentration of the doping atoms.

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